

D–A–D-structured conducting polymer-modified electrodes for detection of lead(II) ions in water

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Abstract Donor–acceptor–donor-structured thiophene derivative-based conducting polymer poly(7,9-dithiophene-2-yl-8*H*-cyclopenta[*a*]acenaphthalene-8-one) was chemically synthesized. This polymer was used to modify both glassy-carbon and carbon-paste electrode, which was used to detect lead(II) ions present in water in the range of 1 mM to 0.1 μ M. Cyclic voltammetry confirms the formation of the co-ordination complex between the soft segment of polymer and the dissolved lead ion. Anodic stripping voltammetry was carried out by the modified electrode to determine the lower limit of detection of dissolved lead(II) species in the solution. Differential adsorptive stripping and impedance measurements were also conducted to find the lowest possible response of the as-synthesized polymer to lead(II) ion in water. The electrochemical performance of the modified electrodes at different pH (4, 7 and 9) environments was carried out by stripping voltammetry, to get optimum sensitivity and stability under these conditions. Finally, interference analysis was carried out to detect the modified electrode's sensitivity towards lead ion affinity in water.

Keywords Donor–acceptor–donor (DAD) · Differential pulse adsorptive stripping voltammetry · Electrochemical impedance · Square-wave voltammetry · Lower limit of detection (LLOD)

1 Introduction

Increasing population and improper handling of the waste has resulted in leaching out hazardous materials into environment [1]. Agricultural activities such as utilization of artificial fertilizers, pesticides, crop preservatives also play a role in adding up of heavy metal ions into the water resources [2]. Carcinogenic metals like Pb^{2+} , Cd^{2+} , Zn^{2+} , Cr^{3+} , Cr^{4+} and Ni^{2+} even in lower ppm exposure causes major health threats to humans [3]. These metals influence damage either by substitution of metals for other elements in biochemical reactions or by binding with vital enzymes which are present in the body. Lead ion is one of the most toxic metal ions to life when its concentrations are at above recommended ppm in the water supplies, food chains and household products. Environmental protection agencies (EPA—USA) recommend water will be potable, if lead ion concentration in water is below 15 ppb. The highly-toxic lead causes serious health and environmental problems. Exposure of lead causes colic, skin pigmentation and necrosis of neurons, axonal degeneration, demyelination, paralysis, cerebral oedema and congestion [4, 5]. Lead salts are considered as hazard class 2 in water and consequently very harmful [6]. Efforts are being made to restrict lead release into the water bodies. In addition to restriction, development of improved sensing methods to detect lead at various sites and environment conditions is also critical. Numerous research works have been carried out on the development of sensors fabricated from solid electrodes functionalized by electroactive polymers [7, 8]. Modifications of electrodes by electroactive polymers to fabricate electrochemical sensors at low cost and ready to use in the systems are interesting option. Various types of conducting polymers such as pyrrole, aniline, carbazole, thiophene, derivatives are used for the fabrication of chemically and

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electrochemically modified electrodes for sensing applications [9–12]. Very few donor–acceptor–donor (DAD)-structured molecules have been used as metal ion sensors. 2,7-Bis(1*H*-pyrrol-2-yl)ethynyl-1,8-naphthyridine was used as a colorimetric sensor for detection of mercuric ion [13] and mono- and bis-(aza-15-crown-5-ether)-substituted DAD dyes for magnesium-ion detection [14].

In the present study, a thiophene derivative 7,9-dithiophene-2yl-8*H*-cyclopenta[*a*]acenaphthalene-8-one (DTCPA) molecule was chemically synthesized as reported elsewhere [15]. The glassy-carbon electrode (GCE) and the carbon-paste electrode (CPE) were modified by this DTCPA polymer. These modified electrodes were used to detect lead ions present in water of the range 10^{-3} – 10^{-7} M by various electrochemical techniques. Analysis of electrochemical response to the presence of lead ion in water at pH 4.0 ± 0.05 has been carried out by cyclic voltammetry (CV), square-wave adsorptive stripping voltammetry (SWASV), differential pulse adsorptive stripping voltammetry (DPASV) and electrochemical impedance spectroscopy (EIS) study. Lower limit of detection (LLOD) of Pb^{2+} from both modified electrodes were determined.

2 Experimental

2.1 Apparatus and reagents

The electrochemical studies were performed with a CHI 660D electrochemical workstation (CH Instruments, USA) in a Faraday cage attached with pico amp current booster. In a three-electrode electrochemical cell, the modified GCE and modified CPE were used as working electrodes (WE). Platinum wire and nonaqueous Ag/Ag^+ electrode were used as counter (CE) and reference electrodes (RE), respectively. Nonaqueous reference electrodes were prepared by mixing 10 mM of silver nitrate (AgNO_3) and 0.1 M (tetrabutylammonium hexafluorophosphate) (TBAPF_6) dissolved in mixture of dichloromethane (DCM) and acetonitrile (1:1). The resulting solution mixture was filled in a RE glass tube and capped with silver wire to form non-aqueous Ag/Ag^+ electrode. The solution mixture was filled to 2/3 of glass tubing volume. The morphology of the cross-sectional surface topography of the electrochemically deposited GCE image was observed using scanning electron microscopy (SEM), which was carried out using ESEM Quanta 200 FEI.

Dicyclohexylcarbodiimide (DCC), 2-thiophene-acetic acid, dimethylaminopyridine (DMAP) and acenaphthenequinone (ANQ), and TBAPF_6 were purchased from Sigma Aldrich and were used without further purification. Graphite powder, solvents—dichloromethane (DCM), acetonitrile (ACN), chloroform and ethanol were procured from local suppliers and these solvents were distilled before use.

Anhydrous ferric chloride and the buffer tablets of pH 4.0 ± 0.05 were obtained from Merck chemicals and were used without further purification.

2.2 Synthesis of 7,9-di(thiophen-2-yl)-8*H*-cyclopenta[*a*]acenaphthylen-8-one (DTCPA)

The intermediate compound, di(thiophen-2-yl)propan-2-one, was synthesized as reported [15, 16]. To a solution mixture of DCC (0.037 mol) and DMAP (0.01 mol) in anhydrous DCM, 2-thiophene-acetic acid (0.035 mol) was added drop wise at 0 °C and stirred for 12 h at room temperature. The obtained products di(thiophen-2-yl)propan-2-one (6.75 mmol) and acenaphthenequinone (6.75 mmol) in ethanol were refluxed for 2 h under inert atmosphere. Potassium hydroxide (0.1 g) dissolved in 3 mL of ethanol was added drop wise to the reaction mixture at room temperature. The obtained dark-green products (DTCPA) were washed with cold ethanol and hot hexane, respectively, and then dried under vacuum.

2.3 Modification of GCE by DTCPA

An electrochemical study in this work has been carried out in a one-compartment cell. The GCE electrode was polished with 1, 0.3 and 0.05 μm size alumina powder, successively. The polished surface was dried under argon to remove residual moisture without damaging the active part of the electrode. Due to insolubility of monomer in aqueous solvent and higher operating voltage of organic electrolytes compared to aqueous electrolyte, electrochemical modification was carried out in non-aqueous solvent as electrolytic solution [17, 18]. TBAPF_6 (0.01 M) was used as supporting electrolyte [19, 20]. Modification of GCE has been carried out by electrochemical polymerization of DTCPA monomer on GCE surface (Fig. 1) by cyclic voltammetry using DCM as solvent. DTCPA monomer of 0.018 g (0.01 M) and 5 mL DCM were mixed in the reaction cell to which supporting electrolyte TBAPF_6 0.19 g (0.1 M) was added and scanned repetitively under the potential range of 1.8 to -1.0 V for 20 cycles with the scan rate of 0.1 V s^{-1} . The electrodeposited poly(DTCPA) (Fig. 1, inset) on the surface of GCE was washed with copious amount of dichloromethane to remove the residual monomer. The modified GCE was dried under vacuum for 1 h at room temperature.

2.4 Preparation of polymer-modified CPE

Poly(DTCPA) was synthesized by oxidative polymerization of DTCPA monomer using anhydrous ferric chloride in chloroform. Modification of CPE was carried out by

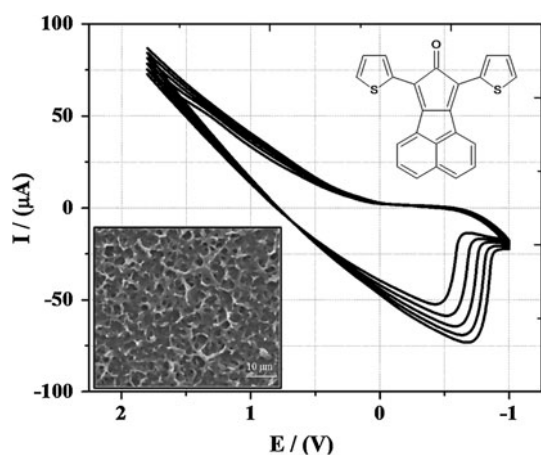


Fig. 1 Cyclic voltammogram while modification of GCE by poly (DTCPA) and surface morphology of the film (inset)

using the fine graphite powder (average particle size $\sim 50 \mu\text{m}$, density 20–30 g/100 mL and >99 % assay) and binder, paraffin oil in the ratio of 4:1. The homogenized paste was packed tightly in a glass tube of 3-mm diameter to form an electrode (WE), and connected to the external circuit through a copper wire. Various percentage of poly(DTCPA) and graphite mixture was evaluated to obtain the maximum voltammetry response for the analyte. For 77:3:20 of graphite:poly(DTCPA):paraffin oil, maximum response was observed. Hence, further analyses were carried out with this optimum composition of the modified electrode. Buffer solutions of $\text{pH } 4.0 \pm 0.05$ were prepared and by using this buffer medium, 1×10^{-3} , 1×10^{-4} , 1×10^{-5} , 1×10^{-6} and 1×10^{-7} M of PbCl_2 solutions were prepared.

3 Results and discussion

Surface imaging was carried out for electrochemically deposited poly(DTCPA) films on GCE. Prior to the SEM analysis, samples were sputter-coated with gold using JEOL (JFC-1100E) ion-sputtering device. Poly(DTCPA) was observed to have circular fibrous network structured morphology (Fig. 1, inset). Morphological study of poly (DTCPA) films suggest that these films display cage type interpenetrating circular network structure. As there is an increase in surface to volume ratio, these type of architecture is ideal for sensing applications [21].

DTCPA, a thiophene derivative, contains two heterocyclic thiophene rings and a ketonic carbonyl group in its backbone. Due to presence of lone pair electron on sulphur, thiophene behaves as an electron-donating moiety. Electron-withdrawing carbonyl group is positioned in between these thiophene rings and the whole molecule resembles the DAD-structure. In this donor–acceptor ensemble, the

electron-withdrawing carbonyl group when exposed to the analyte carbonyl group forms coordination bond with metal cation [22]. However, the lone pair electrons present on sulphur of thiophene group has more influence on metal ion complex formation than acceptor carbonyl group [23]. Hence, the FT-IR spectroscopy analysis suggests that α -position of thiophene ring form coordination bond instead of the carbonyl group, which does not have replaceable protons. Various techniques like CV, SWASV, DPASV and electrochemical impedance were used to characterize and study the sensitivity of modified GCE and CPE towards Pb^{2+} ion in water.

3.1 Voltammetric studies of modified electrodes towards Pb^{2+} ions

Metal-ion sensing capabilities of modified electrode were evaluated by using poly(DTCPA) on GCE surface. CV analysis was performed in the potential range of -1.2 to -0.4 V (Fig. 2), for lead chloride solution of 1×10^{-3} M in buffer solution of pH 4. A sharp lead ion adsorption peak was observed about a potential region of -0.6 V. Furthermore, for PbCl_2 solution of 1×10^{-4} M, the sharp peak was observed again indicating the lead adsorption by the modified GCE. Several measurements were carried out by decreasing the concentrations of lead to determine the limit of lower detection by modified GCE. At concentration lower than 1×10^{-6} M, the significant lead ion peak is not observed by CV technique; however, SWASV (Fig. 4) and DPASV (Fig. 1S) techniques show the response peaks down to the concentration of 1×10^{-7} M. SWASV and DPASV were carried out in the potential range of -1.0 to -0.2 V. Even for lower concentration, response was observed in stripping technique, as it is a

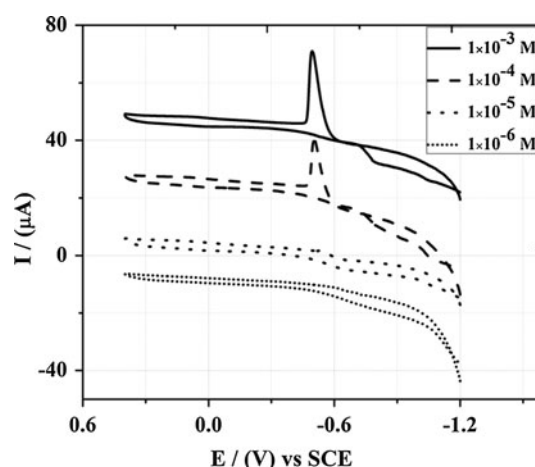


Fig. 2 Cyclic voltammogram for various concentration of PbCl_2 at pH 4 using poly(DTCPA)-modified GCE as working electrode

more sensitive technique compared to potentiodynamic techniques [24–26].

In CPE preparation, poly(DTCPA) blending with graphite will enhance porosity of electrode, and hence assist in metal ion incorporation on to electrode surface [27]. Poly(DTCPA)-modified CPE was analysed by CV technique, which suggests that poly(DTCPA)-modified CPE shows response towards lead ions (Fig. 3). Moreover, poly(DTCPA) which is a conducting polymer, will enhance conductivity of electrode surface; and hence, influence of electrode surface towards metal ion increases [28–30]. DTCPA molecule readily forms complex with metal ion due to presence of thiophene and carbonyl moieties in a single molecule. Other than CV, SWASV (Fig. 5), DPASV (Fig. 2S) and AC impedance techniques were also employed to characterize the response of electrode towards lead ion. It was observed that, SWASV technique presented more assenting results than the DAPSV. Observed peak current and voltage for lead ion indicates the linearity of detection sensitivity with concentration (Figs. 4, inset; 5, inset) for both the electrodes (Table 1) with linear regression value of 0.919 and 0.962, respectively.

3.2 FT-IR analysis of Pb–DTCPA complex

FT-IR spectra of electrochemically polymerized poly (DTCPA) and poly(DTCPA)–Pb complex are as shown in Fig. 6. To prepare poly(DTCPA)–Pb complex, poly (DTCPA)-modified GCE as working electrode was taken in buffer solution (pH 4) which contains lead chloride (10^{-4} M). Using platinum wire as counter electrode and SCE as reference electrode, pre-concentrating step of stripping techniques was carried out for 600 s. Hence, Pb^{2+} ions formed a complex with poly(DTCPA) and was used for analysis by FT-IR. The peaks ~ 2993 , 2892,

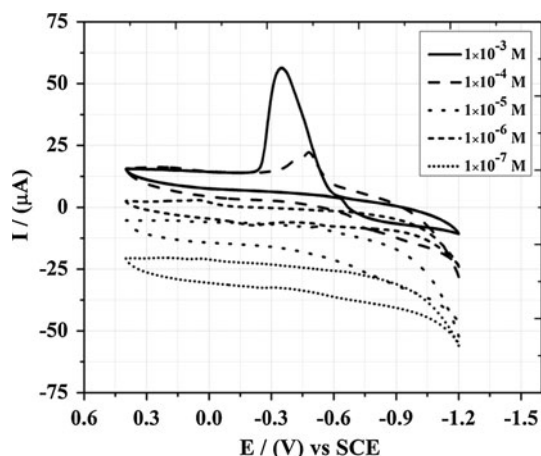


Fig. 3 Cyclic voltammogram for various concentration of PbCl_2 at pH 4 using poly(DTCPA)-modified CPE as working electrode

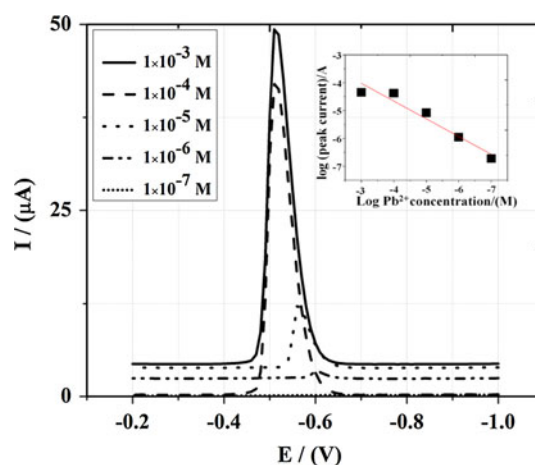


Fig. 4 Square-wave adsorptive stripping voltammetry of PbCl_2 for various concentrations using modified GCE as working electrode and peak current versus concentrations (inset)

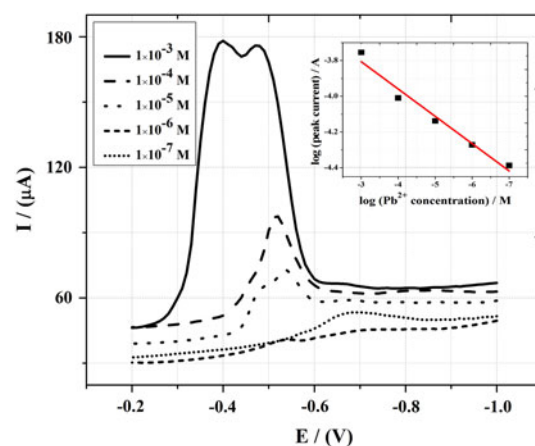


Fig. 5 Square-wave adsorptive stripping voltammetry of PbCl_2 for various concentrations using CPE as a working electrode

2826 cm^{-1} for aromatic C–H stretching were observed in both the neat and complex spectra. The characteristic carbonyl stretching peaks $\sim 1,701\text{ cm}^{-1}$ observed in both neat and complex spectra indicates that carbonyl group of DTCPA molecule does not participate in complex formation with lead. Aromatic C=C stretching peaks were observed at $1,595\text{ cm}^{-1}$. Even though common peaks observed at $1,481\text{ cm}^{-1}$ for aromatic mode, the sharp intensity peaks $\sim 1,331\text{ cm}^{-1}$ which was observed in poly(DTCPA) moiety completely disappeared in poly (DTCPA)-Pb complex indicating that Pb^{2+} forms metal–organic bond at α (position-2 or position-5) to thiophene ring. Hence, at α -position of thiophene ring is electron-rich and readily forms complex with metal cation. The common peaks $\sim 842\text{ cm}^{-1}$ indicate that C–S stretching was observed in both the spectra. Other than these peaks, the common absorbance peaks in the fingerprint region (970,

768 and 697 cm^{-1}) suggest the Pb^{2+} formed complex at thiophene moiety rather than carbonyl moiety.

3.3 Electrochemical impedance spectroscopy (EI) measurement of D–A–D/ Pb^{2+} complexes

EIS technique will be helpful in determining the charge transfer resistance (R_{ct}), ion transport rate and capacitance of modified electrodes accurately [31]. In addition, this technique is a useful tool to determine the minimum concentration level of dissolved heavy metal ions present in the analyte [32]. A small sinusoidal voltage of 5 mV was used to analyse the current response from the electrochemical system. Modified Randle's circuit was employed to model charge transport phenomena as well as the ion diffusion processes at electrode/polymer and polymer/electrolyte interfaces [33].

The Nyquist plot of real and imaginary parts of impedance shows electrode/solution resistance at high

Table 1 Peak current and voltages for various Pb^{2+} concentrations using SWASV for DTCPA-modified GCE and CPE

Sensor	Pb^{2+} concentration (M)	Voltage (V)	Current ($\times 10^{-5}$ A)
DTCPA-modified GCE	10^{-3}	−0.512	4.52
	10^{-4}	−0.517	4.21
	10^{-5}	−0.564	0.840
	10^{-6}	−0.605	0.110
	10^{-7}	−0.625	0.019
DTCPA-modified CPE	10^{-3}	−0.475	17.6
	10^{-4}	−0.517	9.78
	10^{-5}	−0.543	7.28
	10^{-6}	−0.553	5.35
	10^{-7}	−0.689	4.09

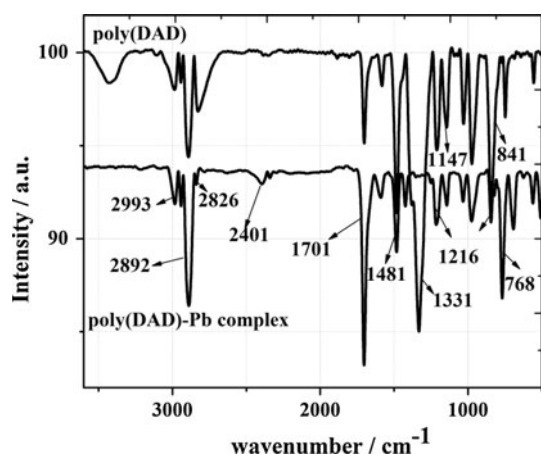


Fig. 6 FT-IR spectra of electrochemically polymerized poly (DTCPA) and lead adsorbed poly(DTCPA)

frequencies (R_s , R_{ct}), redox capacitance at lower frequencies and Warburg impedance at intermediate frequencies (Z_w) [34]. In the case of modified GCE (Fig. 7, top), the solution resistance (R_s) at electrode/polymer interface dominates. This domination results from diffusion controlled process of Pb^{2+} ions at polymer/electrolyte interface by charging the double-layer capacitance (C_{dl}), the linear portion at low frequencies for all concentration of Pb^{2+} ions in the solution. In the case of modified CPE (Fig. 7, bottom), a semi-circle path observed at high frequencies, followed by slope of infinite line at low frequency (diffusion limited process), due to the porosity of the polymer film (thick and thin regions) that is formed during the surface modification of the electrode. An equivalent circuit model for both the diffusion and kinetically controlled reactions is shown in the Fig. 7 (inset). The semi-circle and diffusion-limited (slope lines) in the impedance spectra of Nyquist plot may attributed towards the interaction by the presence of thiophene moieties with Pb^{2+} ions through an intra-molecular charge transfer (CT) process and formation of co-coordinative bond with the Pb^{2+} ions [22]. The linear tailing portion in both the case of modified electrodes suggest a capacitive nature at the electrode/polymer and polymer/solution interface and its low-frequency capacitance value (CLF) can be calculated from Nyquist plot using the relation $\text{CLF} = (2\pi f Z_{\text{im}})^{-1}$ by extrapolating the line at Z_{im} at $f = 1$ Hz. The resulting CLF values for both the electrodes are represented in the Table 2. The CLF value decreases from higher to lower concentration of Pb^{2+} ions in the solution for modified GCE and no remarkable changes were observed in the modified CPE. The charge transfer resistance R_{ct} values for GCE is between 320 and 375 Ω , and for CPE R_{ct} was found to be 121–225 Ω with lowering lead ion concentration (Fig. 7, inset). The observed increment in R_{ct} value for GCE than CPE is mainly due to varied porous nature of CPE, it gives better sensing current for Pb^{2+} ions than GCE (Table 1) [35].

The Bode plot has been evaluated between ($\log |Z|$) and of phase angle (Φ) with a common real-axis of log frequency. The double-layer capacitance (C_{dl}) value can be calculated from the Bode-magnitude plot by extrapolating the line $\log \omega = 0$ and by using the relation $|Z| = 1/C_{\text{dl}}$. The double-layer capacitance value for both modified GCE and CPE, are presented in the Table 2 for the concentrations ranging from 10^{-3} to 10^{-7} M. In the case of modified GCE, the C_{dl} value increases from lower to higher concentration of Pb^{2+} ions. This is due to the charging at the electrode/polymer and polymer/solution interface, which acts as a capacitor at high frequencies, and consequently this value decreases at lower concentration (Fig. 3S). However, in the case of modified CPE, the charging of C_{dl} is not changing steadily from high to low concentration of

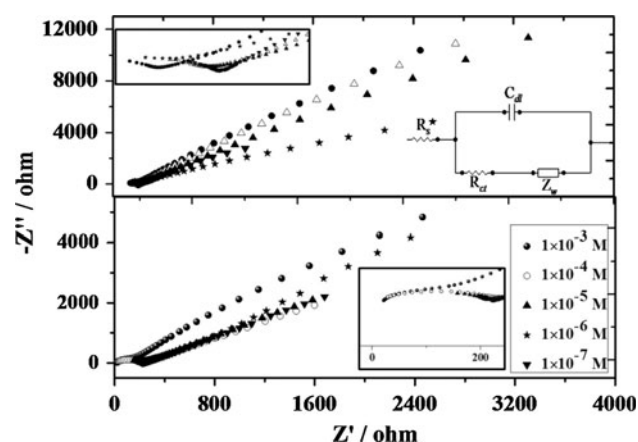


Fig. 7 Nyquist plot for various concentrations PbCl_2 by using modified GCE (top) and CPE (bottom) as working electrode

Table 2 Double-layer capacitance, low-frequency capacitance, and phase angle of DTCPA-modified GCE and DTCPA-modified CPE with various Pb^{2+} concentrations

Sensor	Pb^{2+} concentration (M)	C_{dl} (mF g^{-1})	CLF (mF g^{-1})	Phase angle at 1 Hz ($^\circ$)
DTCPA-modified GCE	10^{-3}	270	100.8	76
	10^{-4}	270	100.8	74
	10^{-5}	263	98.2	72
	10^{-6}	227	85.8	54
	10^{-7}	217	79.3	38
DTCPA-modified CPE	10^{-3}	263	60.0	63
	10^{-4}	263	61.0	38
	10^{-5}	352	56.9	40
	10^{-6}	352	55.8	46
	10^{-7}	357	55.8	40

Pb^{2+} ions (Fig. 5S). This may be due to the poor capacitance build-up at the CPE/polymer interface as high porosity of the solution/polymer interface. From the Bode-phase plot for modified GCE (Fig. 4S) and modified CPE (Fig. 6S) suggests a decreasing phase angle shift (from high to low concentrations of Pb^{2+} ions) of about 76° to 38° (max at 78°) and from 63° and at 40° (max at 76°), both are measured at 1 Hz. The lower phase angle shift observed in the case of modified CPE could be due to the in-homogeneity arising from the porous medium of CPE towards Pb^{2+} ions [36].

3.4 Interference study of modified electrodes

Interference effect of some other heavy metal ions like Cr^{3+} , Hg^{2+} , Cd^{2+} , Co^{2+} and As^{3+} on the response for Pb^{2+} using modified electrodes were analysed (Fig. 8). Only As^{3+} and Cd^{2+} (at above 1×10^{-4} M showed stripping response over

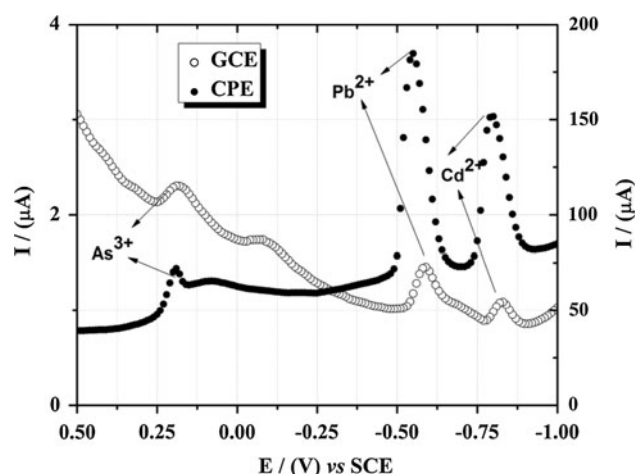


Fig. 8 Interference effect analysis of various heavy metals like Cr^{3+} , Hg^{2+} , Cd^{2+} , Co^{2+} and As^{3+} on the response for Pb^{2+} using poly(DTCPA)-modified electrodes

poly(DTCPA)-modified electrodes. As^{3+} , stripping peak was observed at around $+0.2$ V and which is far away from Pb^{2+} peak (at -0.6 V), and hence these ions show less interference effect over Pb^{2+} . However, Cd^{2+} shows stripping response at -0.8 V has substantial interference effect on Pb^{2+} . From 10^{-4} M CdCl_2 to 10^{-3} M Cd^{2+} considerable increase in the stripping response of lead peak was observed. This indicates that Pb^{2+} mixed with Cd^{2+} can be analysed successfully, if the Cd^{2+} concentration is below 10^{-3} M.

3.5 Optimization of pH

The pH study was carried out for fabricated sensors to optimize the pH at which sensor shows optimum response. Analyses were carried out with pH 4, 7 and 9 (Figs. 7S, 8S). It was observed that poly(DTCPA)-modified GCE and CPE electrodes show optimum response in acidic medium. Poly(DTCPA)-modified GCE shows some response at neutral medium, whereas poly(DTCPA)-modified CPE shows response at pH 9 (Fig. 8S). However, maximum response was observed at acidic medium; hence, fabricated sensors will be useful for detection of Pb^{2+} in acidic medium rather than neutral or basic medium (Fig. 7S).

4 Conclusions

Thiophene derivative with DAD structure was used to modify the glassy-carbon and carbon-paste electrodes and was successfully used as transducer for detecting Pb^{2+} ion in the concentration range of 10^{-3} – 10^{-7} M. The modified electrodes show excellent selectivity towards lead ion present in aqueous solution at $\text{pH } 4 \pm 0.05$. Lead ion in divalent form reacts with DTCPA and forms complex with

the DAD moiety as evidenced by FT-IR results. LLOD of 10^{-7} M from CV and stripping techniques for both modified electrodes was obtained. DTCPA-modified sensors can be used for lead detection in the range of 1×10^{-3} to 1×10^{-7} M. These sensors are easy to fabricate and convenient to use in field.

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